specimens, trench filling initially proceeded with a period of conformal growth followed by the development of sloping sidewalls which may be associated with transient depletion of MBIS within the recessed features. The resulting v-notch growth front then evolved in a manner that is difficult to distinguish from geometric leveling. Stabilization of the feature filling process within the voltammetrically identified critical domain is provided by a decrease in the overpotential for metal deposition that accompanies the flow of current in the resistive electrolyte.

Example 5

[0077] A survey of the effect of various electrolyte additives on the nickel deposition kinetics, as revealed by voltammetric and chrono-amperometric measurements was conducted. The effect of molecular size and function on the metal deposition were examined. Potential suppressor or rate inhibiting species included were dodecyltrimethylammonium chloride [DTAC, $CH_3(CH_2)_{11}N^+(CH_3)_3Cl^-$; manufactured by Fluka], dodecyltrimethylammonium bromide [DTAC, $CH_3(CH_2)_{11}N^+(CH_3)_3Br^-$; manufactured by Fluka]; sodium dodecyl sulfate [SDS, , $CH_3(CH_2)_{11}OSO_3^-Na^+$; manufactured by Fisher], 2-butyne-1,4-diol [2-B-1,4-D, $HOCH_2C{=}CCH_2OH$, manufactured by Aldrich], saccharin [$C_7H_5N0_3S$, manufactured by Aldrich], sodium benzenesulfonate [SBS, $C_6H_5SO_3^-Na^+$, manufactured by Aldrich], cetyltrimethylammonium chloride [CTAC, $CH_3(CH_2)_{15}N^+(CH_3)_3Cl^-$; manufactured by Alfa Aesar], polyethyleneimine $\{PEI,-[NH_2^+CH_2CH_2NH^+(CH_2CH_2NH_3^+)CH_2CH_2^-]_n$, 1800 Mw; branched, manufactured by Fluka Alfa Aesarl}, 4-picoline ($CH_3C_5H_4N$, manufactured by Alfa Aesar), polyethylene glycol [PEG, $(—CH_2CH_2O—)_n$, 3400 Mw; manufactured by Aldrich). Some sulfur-containing organic additives, such as thiourea (TU, H_2NCSNH_2, manufactured by Alfa Aesar), 3-mercapto-1-propane sulfonic acid, sodium salt [MPS, $HS(CH_2)_3SO_3—Na^+$, manufactured by Raschig], bis (3-sulfopropyl) disulfide, sodium salt [SPS, $Na_2^+(SO_3^-(CH_2)_3S)_2$, manufactured by Raschig], and 3-N,N-dimethylaminodithiocarbamoyl-1-propane sulfonic acid, sodium salt [DPS, $Na^+SO_3^-(CH_2)_3SCSN(CH_3)_2$, manufactured by Raschig] were investigated as potential accelerating or depolarizing additives.

[0078] This example shows feature filling with a range of effects on morphological evolution. Filling examples were performed at potentials and current densities where negligible depletion of the nickel cations occurred. The following examples were performed at pH 3, which minimized the parasitic effects of hydrogen evolution on the voltammetric measurements and avoided potential complications associated with the H_2 bubbles that form readily in more acidic electrolytes.

[0079] Ni electrodeposition onto a dielectric substrate metallized with thin Cu seed layer was performed with an electrolytic bath comprising 1 mol/L $NiS0_4.6H_2O$, 0.2 mol/L $NiCl_2.6H_2O$, and 0.5 mol/L H_3B0_3 dissolved in 18 MΩ cm deionized water. A nickel plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The cell for the electrochemical experiments was a Teflon cylinder of 5 cm diameter and 8.5 cm height with parallel, vertically oriented working and counter electrodes separated by a distance of 1.3 cm. The SCE reference electrode was fixed midway between the working and counter electrode but laterally positioned so as not to interfere with the current distribution between the other electrodes. A distance of 1.8 cm separated the working and reference electrode and impedance measurements revealed an uncompensated ohmic resistance of 9.35 Ωcm^2.

[0080] The concentrations of the suppressors were fixed at 100 μmol/L with the exception of PEI which was found to exhibit similar inhibition as the other additives at much lower concentrations. In order to more fully characterize the effect of PEI the concentration was varied from 2 to 200 μmol/L. For comparison to the rate-suppressing additives, accelerating sulfur-bearing species were surveyed using a fixed concentration of 100 μmol/L. Feature filling was examined using Cu-seeded trenches approximately 770 nm deep and 5 μm to 210 nm wide to probe the effect of the suppressing and accelerating additives as well as combinations thereof. Depositions were conducted at -0.9 V vs. SCE for 3 min in the base electrolyte with designated concentrations of the additives. In order to minimize seed-layer corrosion, the specimens were immersed into the electrolyte with the potential applied. Feature filling was also examined as a function of deposition time. Specimen cross sections obtained by mechanical polishing followed by ion milling were examined by field emission scanning electron microscopy (FESEM). A subset of samples was also prepared by a single-step focus ion beam milling and examined by SEM. Filled features were also examined by transmission electron microscopy of cross sections prepared using traditional dimpling and ion-milling methods.

[0081] PEI was shown to exhibit superior void-free feature filling over the other additives screened. For context the results are compared to those obtained from an additive-free nickel plating electrolyte.

[0082] FIG. **11** shows a cross-sectional image of a Ni electrodeposition grown in additive-free solution for 3 min at –0.9 V SCE. Ni was deposited on 5 μm wide trenches **802**, 700 nm wide trenches 804, 400 nm wide trenches **806** and 230 nm wide trenches **808**. The Ni deposit **810** on the 5 μm wide trench **802** was conformal. The slightly smaller thickness **812** on the sidewalls **814** reflects the difference between the seed-layer **816** thickness on the sidewalls **814** versus the free surface **818** and bottom **820** due to line-of-sight constraints during physical vapor deposition (PVD) preparation. The growth front exhibits noticeable roughness **822**. The two widest, low-aspect-ratio trenches **802** and **804** may be void-free while voids **824** are clearly evident in the narrower high-aspect-ratio features of trenches **806** and **808**, shown in FIGS. **11**(*c*) and **11**(*d*).

[0083] Additions of PEI were shown to induce significant changes in the feature-filling dynamics. Conformal filling of an ~1 μm wide trench **902** in the additive-free electrolyte is shown in FIG. **12***a*. The addition of 5 μmol/L PEI yields superconformal film growth, as shown in FIG. **12***b*, by preferential deposition at the bottom **904** and on the deeper sections of the sidewall surfaces **906** of trench **904**, while more limited deposition occurs on the neighboring wall surface **908**. Preferential deposition of nickel is also evident in the bottom corners **910** of the larger features such as that shown in FIG. **12**(*c*). It is shown that void-free filling of the trenches **904** may persists up to an aspect ratio of at least 2.3 for a mid-height trench width greater than 300 nm.

[0084] Ni electrodeposition grown in an electrolytic bath comprising 10 μmol/L PEI for 3 min at –0.9 V showed further evidence of preferential deposition toward the bottoms of the finer features, as shown in FIG. **13**(*a*)-FIG. **13**(*c*). The sloping deposits on the sidewalls **1002** suggests a PEI depletion effect